

Name and DOI of manuscript: Electrochemical Doping in Ordered and Disordered Domains of Organic Mixed Ionic-Electronic Conductors, <https://doi.org/10.1002/adma.202300308>

Data availability

Data measured by the Banerji group in agreement with data management policies (SNF, Horizon 2020...) and shown in the main manuscript is made publicly available in the BORIS repository of the University of Bern. For raw data, S.I. data and data acquired by collaborators, please contact the authors (available upon request).

Data acquisition: Details on the methods of data acquisition are described in the above manuscript and the corresponding S.I.

Data and analysis:

Figure 1

a) Experimental setup for the *in-situ* Vis/NIR spectroelectrochemical measurements. b) Steady-state absorbance spectra of P3HT film (cast from chloroform) in aqueous KPF₆ electrolyte (0.1 mol L⁻¹) upon application of doping voltages ranging from +0.2 V to -0.8 V ($\Delta V = -0.1$ V). The region around 900 nm could not be measured (change between Vis and NIR detector). c) Spectral signature and absorbance cross section of each species obtained from the MCR analysis and d) their corresponding densities as a function of the doping voltage.

Figure 1 data: b) Fig1b_SteadyState.txt

c) Fig1c_SpectralSignatures.txt

d) Fig1d_SpeciesDensity.txt

Person who measured: Priscila Cavassin

Reference to lab book: Notebook Number 1 page 59

Figure 2

a) In-situ electrochemical Raman spectra of P3HT film (cast from chloroform) in aqueous KPF₆ electrolyte (0.1 mol L⁻¹) measured in an 'OECT-like' device with excitation at 633 nm. Experimental spectra (dotted lines) and Gaussian deconvolutions (colored curves) are depicted for voltages applied within regime I (0 V), regime II (-0.5 V) and regime III (-0.8 V). b) Evolution of the relative peak areas of the Raman bands of the different redox species in ordered and disordered domains upon doping from +0.2 V to -0.8 V versus Ag/AgCl ($\Delta V = -0.1$ V). The evolution of the total neutral, polaron and bipolaron population from Vis/NIR spectroelectrochemistry on the same device is shown for comparison.

Figure 2 data: a) Fig_2a_0V.txt, Fig_2a_0.5V.txt, Fig_2a_0.8V.txt

b) Fig2b_RamanPeakAreas_SpeciesDensity.txt

Person who measured: Isabelle Holzer and Priscila Cavassin

Reference to lab book: Notebook Number 1 page 10

Figure 3

Time-resolved species concentrations obtained from VIS/NIR spectroelectrochemistry of a 20 nm P3HT film (cast from chloroform) in aqueous KPF₆ electrolyte (0.1 mol L⁻¹) upon application of a doping voltage step from +0.4 V to a) -0.2 V, b) -0.5 V and c) -0.8 V (left) and a subsequent dedoping voltage back to +0.4 V (right). The dynamics are analysed by kinetic modelling according to the indicated reaction steps (fits shown in black). The simulated ordered (solid line) and disordered (dashed line) subpopulations of polarons (green) and bipolarons (red) are included. For each voltage, a schematic representing the doping in the different morphological domains is depicted (anions in purple and polarons (+) and bipolarons (++) in green).

Figure 3 data: a) Fig_3a_0.2V.txt, Fig3a_0.2V_Dedoping.txt

b) Fig_3b_0.5V.txt, Fig_3b_0.5V_Dedoping.txt

c) Fig_3c_0.8V.txt, Fig_3c_0.8V_Dedoping.txt

Person who measured: Priscila Cavassin

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Figure 4

a) Evolution of the rate constants obtained by kinetic modelling of the species dynamics from the VIS/NIR spectroelectrochemistry data of a 20 nm P3HT film (cast from chloroform) in aqueous KPF₆ electrolyte (0.1 mol L⁻¹). The left side shows the doping processes in the ordered and disordered regions of P3HT as a function of oxidation voltage, while the right side shows the corresponding dedoping processes as a function of the initial oxidation voltage (before dedoping to +0.4 V). b) Dependence of the doping equilibrium constants (from the kinetic modelling) on the applied oxidation voltage.

Figure 4 data: a) Figure4a_RateConstants.txt

b) Figure4b_EquilibriumConstants.txt

Person who measured: Priscila Cavassin

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Figure 5

a) MCR species densities as a function of doping voltage for regioregular P3HT films cast from 1,2-dichlorobenzene (DCB, squares with dashed lines) and chloroform (CF, circles with solid lines), from VIS/NIR spectro-electrochemistry in aqueous KPF₆ electrolyte (0.1 mol L⁻¹) measured in 'OECT-like' devices. b) Steady-state absorbance spectra of a 120 nm regiorandom RRa-P3HT film cast on ITO substrate upon application of doping voltages ranging from -0.7 V to -1.4 V ($\Delta V = -0.1$ V) in KPF₆/acetonitrile electrolyte. c) Corresponding spectral signatures of each species obtained from the MCR analysis. d) Time-resolved species concentrations obtained for the RRa-P3HT film upon application of (left) a doping voltage of -1.2 V and (right) a dedoping voltage of 0 V. For comparison, the doping dynamics at -0.6 V (similar overpotential) of a regioregular P3HT film (rr-P3HT) cast from chloroform are shown.

Figure 5 data: a) Fig5a_SpeciesDensity.txt

b) Fig5b_SteadyStateRRa.txt

c) Fig5c_SpectralSignatures.txt

d) Fig5d_Dynamics_doping.txt, Fig5d_Dynamics_doping.txt

Person who measured: Priscila Cavassin

Reference to lab book: Notebook Number 1 page 68

Figure 6

a) THz conductivity parameters obtained *in-situ* for a ~270 nm thick regioregular P3HT film cast from 1,2-dichlorobenzene in an OECT-like device in TBAPF₆/acetonitrile electrolyte. The real conductivity at 1 THz (top), the effective mobility obtained from Drude-Smith analysis (middle), and the density of conductive charges (also from Drude-Smith analysis, bottom) are shown as thick black lines with round markers. In addition, the density of the different redox species (from Vis/NIR spectroelectrochemistry and MCR analysis on the same device) is indicated at the bottom. The total injected charge density is calculated as the polaron plus twice the bipolaron density (P+2B). b) Real conductivity at 1 THz as a function of conductive charge density. c) Fraction of charge in bipolarons (2B/(2B+P)) as a function of the injected charge density. d) Fraction of conductive charge as a function of the fraction of charge in bipolarons. Solid lines in b)-d) are guides to the eye.

Figure 6 data: a) Fig6a_Thz.txt

b) Fig6b_Conductivity.txt

c) Fig6c_BipolaronChargeFraction.txt

d) Fig6d_ChargeFraction.txt

Person who measured: Demetra Tsokkou

Reference to lab book: Notebook Number 5, page 44 (07/07/21)